Cleavage of Carbon−Sulfur Bonds by Triosmium Clusters. Evidence for a Novel Two-Center Mechanism Predicated on Metal−Metal Bond Cleavage

Richard D. Adams,* O-Sung Kwon, and Joseph L. Perrin

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

Received January 6, 2000

Summary: The 2-vinylthiacyclohexane cluster complex $Os_3(CO)_{10}[\mu\text{-}\eta^3\text{-}S(CH_2)_4CHCHCH_2]$ *(**1**) is transformed into the complex* $Os_3(CO)_{10}[\mu\text{-}\eta^4\text{-}S(CH_2)_4CHCHCH_2]$ *(**2**) by a ring-opening cleavage of one carbon−sulfur bond, a CO ligand shift, and opening of the cluster. Compound **2** is converted into the complexes* $Os_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2C(H){=}C(H)C(H){=}CH_2](\mu\text{-}H)$ *(**3**) and* $Os_3(CO)_9[\mu\text{-}\eta^4\text{-}cis\text{-}S(CH_2)_4CHCHCH_2]$ *(**4**) by re-forming the metal−metal bond. Compound **4** isomerizes to* $Os_3(CO)_9[\mu\text{-}\eta^4\text{-}trans\text{-}S(CH_2)_4CHCHCH_2]$ *(**5**).*

Cooperative interactions between metal atoms are one of the important features that distinguish organic transformations of polynuclear metal complexes and bimetallic catalysts from those of their mononuclear counterparts.[1−3] Bridging coordination of ligands is one of the most common ways metal clusters can activate small molecules.[2] The making and breaking of metal−metal bonds are also known to be important processes for the introduction of small organic molecules into polynuclear metal complexes.[3] We have now found evidence for an unusual metal−metal bond cleavage process involved in a ring-opening carbon−sulfur bond cleavage reaction of a cyclic thioether ligand in a triosmium cluster complex.

The compound $Os_3(CO)_{10}[\mu\text{-}\eta^3\text{-}\overline{S(CH_2)_4C}HCHCH_2]$ (**1**) was obtained in 54% yield from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with 2-vinylthiacyclohexane (VTH) at 25 °C after 19 h.[4] Compound **1** contains a VTH ligand bridging the edge of the triangular triosmium cluster with the sulfur atom coordinated to one metal atom and the vinyl group to the other (see Figure 1).[5] When it is heated to 45 °C for 40 h, compound **1** is transformed into the four new compounds $Os_3(CO)_{10}[\mu\text{-}\eta^4\text{-}S(CH_2)_4CHCHCH_2]$ (**2**; 8% yield), $Os_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2C(H){=}C(H)C(H){=}CH_2](\mu\text{-}H)$ (**3**; 16%), $Os_3(CO)_9[\mu\text{-}\eta^4\text{-}cis\text{-}S(CH_2)_4CHCHCH_2]$ (**4**; 10%), and $Os_3(CO)_9[\mu\text{-}\eta^4\text{-}trans\text{-}S(CH_2)_4CHCHCH_2]$ (**5**; 3%).[6] Compound **2** is converted directly into **3** (44% yield), **4** (20%), and **5** (13%) when heated, but not back into **1**. Compounds **2**, **4**, and **5** have been characterized crystallographically.

Compound **2** is an isomer of **1** formed by an opening of the VTH ring through the cleavage of the carbon−sulfur bond to the vinyl-substituted carbon atom (see Figure 2). The cluster of **2** has also been opened, and a thiolato sulfur atom bridges the two nonbonded osmium atoms. The vinyl group and its neighboring carbon atom are bonded to one osmium atom in an η^3-allylic fashion. Most important is the distribution of the 10 CO ligands in **2**; that is, 2 of the osmium atoms have 4 carbonyl ligands while the third one has only 2. This will have important mechanistic implications (see below). Compound **4** is formed from **2** by loss of one CO ligand and formation of a metal−metal bond between the two

---

[1] (a) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169. (b) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167. (c) Esteruelas, M. A.; Garcia, M. P.; Lopez, A. M.; Oro, L. A. *Organometallics* **1991**, *10*, 127. (d) Hostetler, M. J.; Butts, M. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 2743. (e) Choukroun, R.; Gervais, D.; Jaud, J.; Kalck, P.; Senocq, F. *Organometallics* **1986**, *5*, 67.

[2] (a) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91. (b) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451. (c) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, *84*, 959.

[3] (a) Johnson, B. F. G.; Roberts, Y., *J. Cluster Sci.* **1993**, *4*, 231. (b) Johnson, B. F. G.; Lewis, J.; Pippard, D., *J. Organomet. Chem.* **1978**, *160*, 263. (c) Darensbourg, D. J. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990; Chapter 4. (d) Huttner, G.; Knoll, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 743. (e) Huttner, G.; Schneider, J.; Müller, H. D.; Mohr, G.; von Seyerl, J.; Wohlfart, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 76.

[4] Compound **1** was obtained in 54% yield from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with 2-vinylthiacyclohexane in CH_2Cl_2 after 19 h at 25 °C. It was isolated by TLC using hexane solvent. For **1**: IR (ν(CO) (cm^{-1}) in hexane) 2105 (m), 2044 (m), 2032 (s), 2017 (vs), 1997 (m), 1983 (w), 1969 (m), 1962(m). ^{1}H NMR (δ in CDCl$_3$) 2.91 (dd, J_{H-H} = 23 Hz, J_{H-H} = 23 Hz, 2H), 2.77 (bm, 1H), 2.64 (m, 1H), 2.31 (m, 1H), 2.11 (dd, J_{H-H} = 2 Hz, J_{H-H} = 11 Hz, 1H), 2.07−1.66 (bm, 5H), 1.42 (bm, 1H).

[5] Crystal data for **1**: $Os_3SO_{10}C_{17}H_{12}$, M_r = 978.94, space group $P2_1/c$, a = 12.368(6) Å, b = 12.692(3) Å, c = 29.491(9) Å, β = 100.08(4)°, V = 4558(3) Å^3, Z = 8, μ = 16.815 mm^{-1}, λ(Mo Kα) = 0.710 73 Å, T = 20 °C, 3410 reflections ($I > 3.00\sigma(I)$); Lorentz/polarization and absorption corrections (DIFABS) applied; solved by direct methods (SIR92); 555 variables refined, full matrix on F, R1 = 0.055, wR2 = 0.073, GOF = 1.49; two structurally similar independent molecules in the asymmetric crystal unit.

[6] When it was heated to 45 °C for 40 h in a hexane solution, **1** was converted into **2** (8% yield), **3** (16%), **4** (10%), and **5** (3%). When it was heated to 50 °C in hexane solvent for 48 h, compound **2** was transformed into **3**, (44% yield), **4**, (20%), and **5** (13%). For **2**: IR (ν(CO) (cm^{-1}) in hexane) 2123 (m), 2066 (s), 2047 (vs), 2018 (s), 2004 (w), 1995 (s), 1983 (m), 1927 (m).; ^{1}H NMR (δ in CDCl$_3$) 4.66 (dt, J_{H-H} = 12 Hz, J_{H-H} = 15 Hz, 1H), 4.17 (m, 1H), 3.62 (dt, J_{H-H} = 7 Hz, J_{H-H} = 4 Hz, 1H), 2.78 (m, 1H), 2.46 (m, 2H), 2.13 (m, 1H), 1.65 (m, 2H), 1.51 (dd, J_{H-H} = 12 Hz, J_{H-H} = 2 Hz, 1H), 1.32 (m, 2H). For **3**: IR (ν(CO) (cm^{-1}) in hexane) 2109 (m), 2067 (vs), 2059 (s), 2025 (vs), 2019 (s), 200 (w), 1999 (s), 1990 (m), 1983 (m); ^{1}H NMR (δ in CDCl$_3$) 6.27 (dt, J_{H-H} = 19 Hz, J_{H-H} = 21 Hz, 1H), 6.04 (dd, J_{H-H} = 10 Hz, J_{H-H} = 15 Hz, 1H), 5.61 (dt, J_{H-H} = 15 Hz, J_{H-H} = 15 Hz, 1H), 5.10 (d, J_{H-H} = 17 Hz, 1H), 4.98 (d, J_{H-H} = 10 Hz, 1H), 2.34 (t, J_{H-H} = 16 Hz, 2H), 2.18 (q, J_{H-H} = 7 Hz, 2H), 1.68 (m, 2H), −17.40 (s, 1H). For **4**: IR (ν(CO) (cm^{-1}) in hexane) 2098 (m), 2049 (s), 2021 (vs), 2014(m), 1999 (m), 1976 (m), 1928 (w); ^{1}H NMR (δ in CDCl$_3$): 4.87 (m, 1H), 4.66 (m, 1H), 4.29 (dt, J_{H-H} = 7 Hz, J_{H-H} = 3 Hz, 1H), 3.68 (bd, J_{H-H} = 12 Hz, 1H), 2.95 (m, 1H), 2.44 (dd, J_{H-H} = 2 Hz, J_{H-H} = 13 Hz, 1H), 2.15 (m, 1H), 1.79 (m, 1H), 1.68 (m, 4H). For **5**: IR (ν(CO) (cm^{-1}) in hexane) 2097 (m), 2050 (s), 2019 (vs), 2013 (m), 1998 (m), 1978 (m), 1908 (w); ^{1}H NMR (δ in CDCl$_3$) 4.59 (dt, J_{H-H} = 8 Hz, J_{H-H} = 22 Hz, 1H), 4.18 (dt, J_{H-H} = 9 Hz, J_{H-H} = 6 Hz, 1H), 3.15 (dd, J_{H-H} = 3 Hz, J_{H-H} = 8 Hz, 1H), 3.07 (dt, J_{H-H} = 18 Hz, J_{H-H} = 5 Hz, 1H), 2.87 (ddd, J_{H-H} = 1 Hz, J_{H-H} = 10 Hz, J_{H-H} = 14 Hz, 1H), 2.34 (m, 2H), 2.09 (m, 1H), 1.80 (m, 2H), 1.23 (m, 1H), 0.78 (m, 1H).

10.1021/om0000111 CCC: $19.00

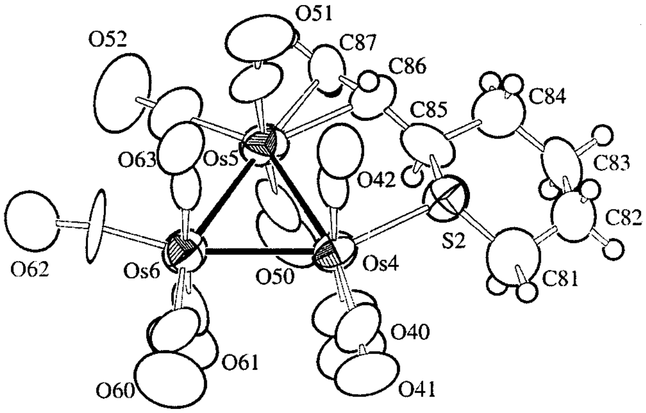


Figure 1. ORTEP diagram of the molecular structure of $Os_3(CO)_{10}(\mu\text{-}\eta^3\text{-}\overline{S(CH_2)_4C}HCHCH_2)$ (**1**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) (values for molecule 2 are given in brackets): Os(1)−Os(2) = 2.871(2), Os(1)−Os(3) = 2.837(2), Os(2)−Os(3) = 2.900(2), Os(1)−S(1) = 2.381(8), Os(2)−C(76) = 2.28(3), Os(2)−C(77) = 2.21(3), S(1)−C(75) = 1.88(3) [Os(4)−Os(5) = 2.867(2), Os(4)−Os(6) = 2.844(2), Os(5)−Os(6) = 2.905(2), Os(4)−S(2) = 2.39(1), Os(5)−C(86) = 2.26(4), Os(5)−C(87) = 2.23(3), S(2)−C(85) = 1.88(3)].

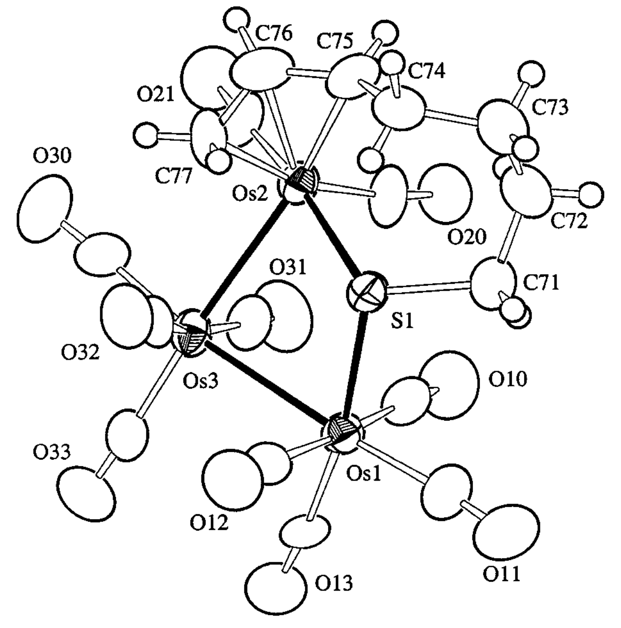
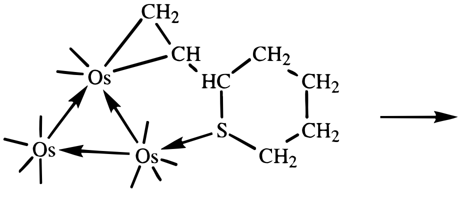


Figure 2. ORTEP diagram of the molecular structure of $Os_3(CO)_{10}[\mu\text{-}\eta^4\text{-}S(CH_2)_4CHCHCH_2]$ (**2**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å): Os(1)···Os(2) = 3.954(1), Os(1)−Os(3) = 2.953(1), Os(2)−Os(3) = 2.926(1), Os(1)−S(1) = 2.433(5), Os(2)−S(1) = 2.471(5), Os(2)−C(75) = 2.32(2), Os(2)−C(76) = 2.22(2), Os(2)−C(77) = 2.28(2), S(1)−C(71) = 1.87(2).

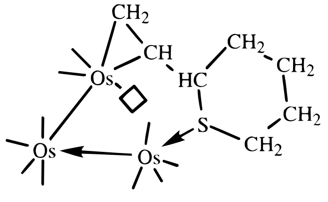
nonbonded osmium atoms. Compound **5** is derived from **4** by a simple *syn*−*anti* isomerization in the η^3-allylic portion of the thiolate ligand.

The structure of **3** was established by spectral comparisons to the related compound $Os_3(CO)_{10}[\mu\text{-}SCH_2CH_2C(H){=}C(H)C(H){=}CH_2](\mu\text{-}H)$, which was obtained from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with 2-vinyltetrahydrothiophene and was structurally characterized.[8] Compound **3** contains a conjugated diene group at the end of a trimethylene chain that is linked to the cluster through a thiolate sulfur atom.

The interrelationships of the various products are shown in Scheme 1. Compound **2** appears to be an intermediate en route to **3**−**5**, and the mechanism of its formation is central to understanding the ring-opening carbon−sulfur bond cleavage process. We observed that compound **2** is not formed from **4** under 1 atm of CO under the reaction conditions. It thus appears that **2** is formed from **1** *without* loss of CO. This could be achieved by a shift of a CO ligand from the vinyl-coordinated osmium atom to the sulfur-coordinated osmium atom in **1**. One could imagine an intermediate with a structure such as **A** containing a network of



A



B

heteropolar metal−metal bonds. Opening of one of the metal−metal bonds could lead to an intermediate such as **B** containing a vacant coordination site on the vinyl coordinated osmium atom. This metal atom could then insert into the carbon−sulfur bond to yield **2**.

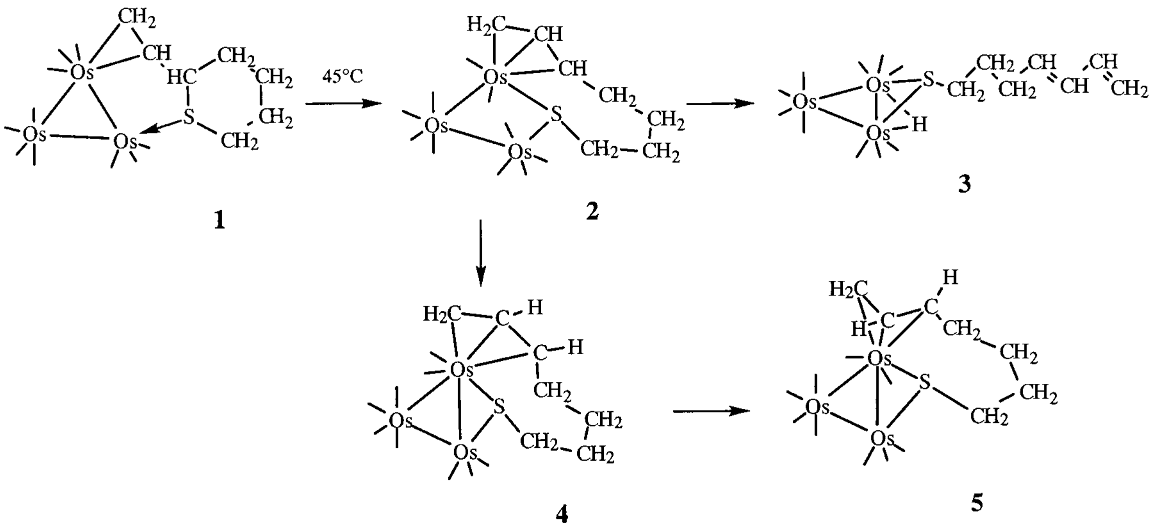
Cleavage of heteropolar metal−metal bonds has been proposed previously as a mechanism for generation of vacant coordination sites to facilitate the addition of certain ligands to metal carbonyl cluster complexes.[3a,b] The unexpected feature of the transformation of **1** to **2** is that the CO ligand was shifted to a neighboring metal atom and the metal−metal bond is then opened to formally provide a “vacant” coodination site where carbon−sulfur bond cleavage can then occur. In reality, the sequence of transformations described above may be more concerted than stepwise, and this description is presented more for the purpose of understanding the course of events rather than to imply the existence of a discrete intermediate such as **B**.

---

[7] Crystal data for **2**: $Os_3SO_{10}C_{17}H_{12}$, M_r = 978.94, space group $P2_1/n$, a = 14.770(4) Å, b = 10.015(4) Å, c = 16.402(7) Å, β = 113.80(4)°, V = 2220(2) Å^3, Z = 4, μ = 17.26 mm^{-1}, λ(Mo Kα) = 0.710 73 Å, T = 20 °C, 1812 reflections ($I > 3.00\sigma(I)$); Lorentz/polarization and absorption corrections (DIFABS) applied; solved by direct methods (SIR92); 281 variables refined, full matrix on F, R1 = 0.031, wR2 = 0.033, GOF = 1.03. Crystal data for **4**: $Os_3SO_9C_{16}H_{12}$, M_r = 950.93, space group $P2_1/n$, a = 15.553(5) Å, b = 14.966(9) Å, c = 9.238(4) Å, β = 90.664(9)°, V = 2150(2) Å^3, Z = 4, μ = 17.81 mm^{-1}, λ(Mo Kα) = 0.710 73 Å, T = 20 °C, 1661 reflections ($I > 3.00\sigma(I)$); Lorentz/polarization and absorption corrections (DIFABS) applied; solved by direct methods (SIR92); 263 variables refined, full matrix on F, R1 = 0.036, wR2 = 0.046, GOF = 1.18. Crystal data for **5**: $Os_3SO_9C_{16}H_{12}$, M_r = 950.93, space group $P2_1/a$, a = 13.385(5) Å, b = 21.51(1) Å, c = 14.635(4) Å, β = 93.76(4)°, V = 4205(2) Å^3, Z = 8, μ = 18.22 mm^{-1}, λ(Mo Kα) = 0.710 73 Å, T = 20 °C, 2990 reflections ($I > 3.00\sigma(I)$); Lorentz/polarization and absorption corrections (DIFABS) applied; solved by direct methods (SIR92), 519 variables refined, full matrix on F, R1 = 0.037, wR2 = 0.045, GOF = 1.07.

[8] Adams, R. D.; Kwon, O. S.; Perrin, J. L. *J. Organomet. Chem.* **1999**, *584*, 223.

Scheme 1



The formation of compound **3** appears to lie on a pathway that differs from that of the formation of **4** and **5**, since these compounds cannot be interconverted. Compound **3** could be formed from **2** by C−H bond cleavage and the formation of a metal−metal bond that induces the release of the diene grouping without loss of CO.

The cleavage of carbon−sulfur bonds is a key step in the hydrodesulfurization of the organosulfur compounds found in fossil fuels.[9] Polynuclear metal complexes have been shown to exhibit a superior ability to cleave carbon−sulfur bonds.[10,11] We have recently characterized a variety of carbon−sulfur bond cleavage reactions for sulfur heterocycles coordinated to metal cluster complexes.[11] We have also shown that a vinyl substituent α to the sulfur atom promotes ring-opening carbon−sulfur bond cleavage reactions for certain heterocycles.[8] As implied by the above results, coordination of the vinyl group may be important to this process.

The cleavage of metal−metal bonds has been observed in the cleavage of phosphorus−carbon bonds by metal clusters.[12] Metal−metal bond cleavage processes may be a common feature of the mechanisms of heteroatom−carbon bond cleavages at multinuclear metal sites.

Acknowledgment. This research was supported by the National Science Foundation.

Supporting Information Available: Text giving experimental details of the syntheses and tables of final atomic coordinates, bond distances and angles, and anisotropic thermal parameters for the structural analyses of **1**, **2**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0000111

---

[9] (a) Startsev, A. N. *Catal. Rev.-Sci. Eng.* **1995**, *37*, 353. (b) Schuman, S.; Shalit, H. *Catal. Rev.* **1970**, *4*, 245. (c) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1978; Chapter 5. (c) Massoth, F. E. *Adv. Catal.* **1978**, *27*, 265. (d) Prins, R.; De Beer, V. H. H.; Somorjai, G. A. *Catal. Rev.-Sci. Eng.* **1989**, *31*, 1. (e) Kwart, H.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* **1980**, *61*, 128. (f) Curtis, M. D.; Penner-Hahn, J. E.; Schwank, J.; Beralt, O.; McCabe, D. J.; Thompson, L.; Waldo, G. *Polyhedron* **1988**, *7*, 2411. (g) Curtis, M. D. *Appl. Organomet. Chem.* **1992**, *6*, 429. (h) Gates, B. C.; Topsoe, H. *Polyhedron* **1997**, *16*, 3213. (i) Friend, C. M.; Roberts, J. T. *Acc. Chem. Res.* **1988**, *21*, 394.

[10] (a) Riaz, U.; Curnow, O. J.; Curtis, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 4357. (b) Jones, W. D.; Chin, R. M. *J. Am. Chem. Soc.* **1994**, *116*, 198. (c) Chen, R.; Angelici, R. J. *Appl. Organomet. Chem.* **1992**, *6*, 479. (d) Luo, S.; Ogilvy, A. E.; Rauchfuss, T. B. *Organometallics* **1992**, *10*, 1002.

[11] (a) Adams, R. D.; Pompeo, M. P.; Wu, W.; Yamamoto, J. H. *J. Am. Chem Soc.* **1993**, *115*, 8207. (b) Adams, R. D.; Pompeo, M. P. *Organometallics* **1992**, *11*, 103. (c) Adams, R. D.; Pompeo, M. P. *Organometallics* **1992**, *11*, 2281. (d) Adams, R. D.; Belinski, J. A.; Pompeo, M. P. *Organometallics* **1992**, *11*, 2016. (e) Adams, R. D.; Belinski, J. A.; Schierlmann, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 9004.

[12] Bergounhou, C.; Bonnet, J.-J.; Fompeyrine, P.; Lavigne, G.; Lugan, N.; Mansilla, F.